ISSN 0020-1685, Inorganic Materials, 2009, Vol. 45, No. 6, pp. 689–693. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © L.A. Trusov, D.D. Zaitsev, P.E. Kazin, Yu.D. Tret'yakov, M. Jansen, 2009, published in Neorganicheskie Materialy, 2009, Vol. 45, No. 6, pp. 749–753.

Preparation of Magnetic Composites through $SrO–Fe_2O_3–Al_2O_3–B_2O_3$ Glass Crystallization

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Received October 8, 2008

Abstract—Glasses with nominal compositions $11SrO \cdot 5.5Fe_2O_3 \cdot 4.5Al_2O_3 \cdot 4B_2O_3$ (1) and $15SrO \cdot 5.5Fe_2O_3 \cdot 4.5Al_2O_3 \cdot 4B_2O_3$ (2) were prepared by rapidly quenching oxide melts between counterrotating steel rollers. The glasses were then heat-treated in the range 650–950°C to produce glass-ceramic samples. The samples were characterized by X-ray diffraction, electron microscopy, and magnetic measurements. The phase composition of the glass-ceramics was determined, and their microstructure and magnetic properties were studied. The annealing temperature was shown to have a strong effect on the coercivity of the materials, which reaches 650 and 570 kA/m for compositions 1 and 2, respectively.

DOI: 10.1134/S0020168509060193

INTRODUCTION

Strontium and barium *M* hexaferrites are used in the fabrication of permanent magnets. They offer the advantages of high magnetocrystalline anisotropy, considerable coercivity, chemical stability, and relatively low cost [1]. Materials based on single-domain hexaferrite particles possess the highest coercivity. One convenient technique for the synthesis of such particles is oxide glass crystallization driven by heat treatment [2]. This approach offers the possibility to control the size and shape of forming hexaferrite particles by varying the glass composition and annealing conditions and to dope the material.

In a recent report [3], we described the preparation of magnetic glass-ceramics based on aluminum-doped strontium hexaferrite through $13SrO \cdot 5.5Fe_2O_3 \cdot 4.5Al_2O_3 \cdot 4B_2O_3$ glass crystallization. We obtained samples with the highest coercivity among hexaferrites: above 800 kA/m. In this paper, we examine the effect of strontium content on the magnetic properties of $SrO–Fe_2O_3–Al_2O_3–B_2O_3$ glass-ceramics.

EXPERIMENTAL

Glass samples with nominal compositions $11SrO \cdot 5.5Fe_2O_3 \cdot 4.5Al_2O_3 \cdot 4B_2O_3$ (1) and $15SrO \cdot 5.5Fe_2O_3 \cdot 4.5Al_2O_3 \cdot 4B_2O_3$ (2) were prepared by quenching oxide melts. The starting chemicals used were iron(III) oxide (Fe_2O_3), strontium carbonate ($SrCO_3$), boric acid (H_3BO_3), and aluminum oxide (Al_2O_3) (all of reagent grade). The starting mixtures were first reacted at 700°C for 3 h. The resultant powders were melted in a tube furnace at 1400°C. After a 2-h hold, the melts were quenched in water between counterrotating steel rollers to give glasses.

To produce glass-ceramics, the glasses were crammed for 2 h at temperatures from 600 to 950° in a preheated furnace and then quenched in air.

X-ray diffraction (XRD) characterization was carried out with an Enraf-Nonius FR-552 Guinier focusing camera ($Cu\,K_{\alpha_1}$ radiation). In magnetic measurements, we used a Quantum Design SQUID magnetometer (magnetic fields up to 5 T) and purpose-designed Faraday balance (magnetic fields up to 0.9 T). Microstructures were examined on a Leo Supra 50VP scanning electron microscope (SEM) equipped with an electron probe X-ray microanalysis system.

RESULTS AND DISCUSSION

XRD examination showed that all of the glass samples were fully amorphous. The XRD data for the glass-ceramics are presented in Table 1. Crystalline phases appeared at annealing temperatures above 700°C. The following phases were identified in our samples: strontium orthoferrite, $SrFeO_{3-y}$; strontium aluminate, $SrAl_2O_4$; strontium borate, $Sr_2B_2O_5$; and strontium hexaferrite, $SrFe_{12}O_{19}$. The diffraction peaks from strontium hexaferrite and strontium aluminate were markedly shifted, suggesting partial substitution of aluminum for iron in $SrFe_{12}O_{19}$ (reduction in unit-cell parameters) and iron for aluminum in $SrAl_2O_4$ (increase in unit-cell parameters).

The first, weak XRD peaks of strontium hexaferrite appeared at 750 and 700°C for compositions 1 and 2, respectively. At low annealing temperatures, the major

Table 1. XRD data for the glass-ceramic samples prepared from glasses 1 and 2

Annealing temperature, °C	Crystalline phases	
	1	2
650	–	–
700	$SrFeO_{3-y}$	$SrFeO_{3-y}$, $SrAl_2O_4$,$SrFe_{12}O_{19}$ (traces)
750	$SrFeO_{3-y}$, $SrAl_2O_4$, $SrFe_{12}O_{19}$ (traces)	$SrFeO_{3-y}$, $SrAl_2O_4$, $Sr_2B_2O_5$ (traces), $SrFe_{12}O_{19}$ (traces)
800	$SrFeO_{3-y}$ (traces), $SrAl_2O_4$, $Sr_2B_2O_5$, $SrFe_{12}O_{19}$	$SrFeO_{3-y}$, $SrAl_2O_4$, $Sr_2B_2O_5$ (traces), $SrFe_{12}O_{19}$ (traces)
850, 900, 950	$SrAl_2O_4$, $Sr_2B_2O_5$, $SrFe_{12}O_{19}$	$SrFeO_{3-y}$, $SrAl_2O_4$, $Sr_2B_2O_5$, $SrFe_{12}O_{19}$

Table 2. Hexaferrite cell parameters and degree of aluminum substitution for iron in glass-ceramic samples

Glass composition	Annealing temperature, °C	a, Å	c, Å	V, Å^3	Degree of substitution, x
1	850	5.830(4)	22.85(1)	672.6(8)	2.1 ± 0.1
	900	5.830(1)	22.846(3)	672.7(1)	
	950	5.832(1)	22.89(1)	674.2(3)	
2	850	5.861(2)	22.94(5)	682.5(0)	1.1 ± 0.1
	900	5.859(1)	22.95(2)	682.3(3)	
	950	5.852(1)	22.962(8)	680.9(4)	1.3 ± 0.1

Fe-containing phase was $SrFeO_{3-y}$. In the samples of composition 2, the orthoferrite was present at all annealing temperatures. In the samples of composition 1, it was only present after annealing in the range 750–800°C. Above 800°C, only trace levels of this phase were detectable, and the major Fe-containing phase was strontium hexaferrite. For both compositions, the peaks from the hexaferrite were very broad at annealing temperatures of up to 800°C, attesting to a small particle size of the hexaferrite in those samples.

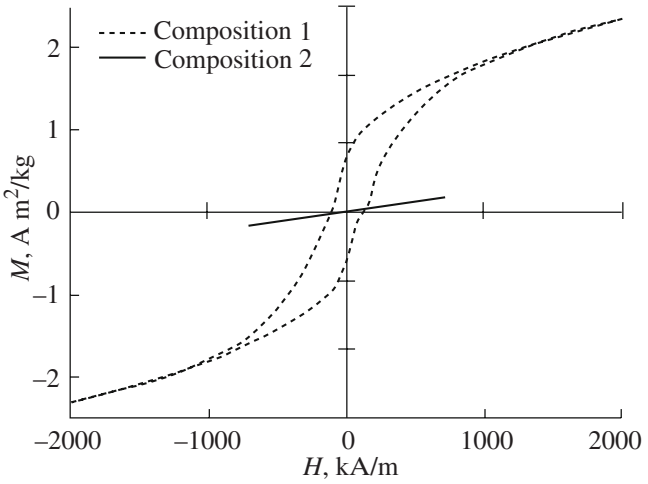

Fig. 1. $M(H)$ plots of glasses 1 and 2.

The unit-cell parameters of strontium hexaferrite in the glass-ceramics prepared at 850, 900, and 950°C are listed in Table 2. From the dependence of the unit-cell parameters on aluminum content, one can evaluate the degree of substitution, x, in $SrFe_{12-x}Al_xO_{19}$ [4, 5]. The XRD peaks of the hexaferrite were very broad, which affected the measurement accuracy. The degree of aluminum substitution for iron was found to drop with increasing strontium content and to slightly increase with annealing temperature (Table 2).

The magnetization M of glass 2 is a linear function of magnetic field (Fig. 1); that is, this glass is a paramagnet. In an applied field of 700 kA/m, its magnetization is 0.2 A m^2/kg. The $M(H)$ data for glass 1 are also presented in Fig. 1. The observed magnetic hysteresis indicates that the as-prepared glass contained a ferromagnetic impurity. Assuming that the glass contained strontium hexaferrite with a saturation magnetization of 74 A m^2/kg [4], we obtain that the ferromagnetic content of the as-prepared glass 1 is within 3 wt %.

Figures 2 and 3 illustrate the magnetic properties of the glass-ceramics. The saturation magnetization M_s is proportional to the amount of strontium hexaferrite produced by annealing, whereas aluminum substitution for iron reduces the magnetization [4, 6].

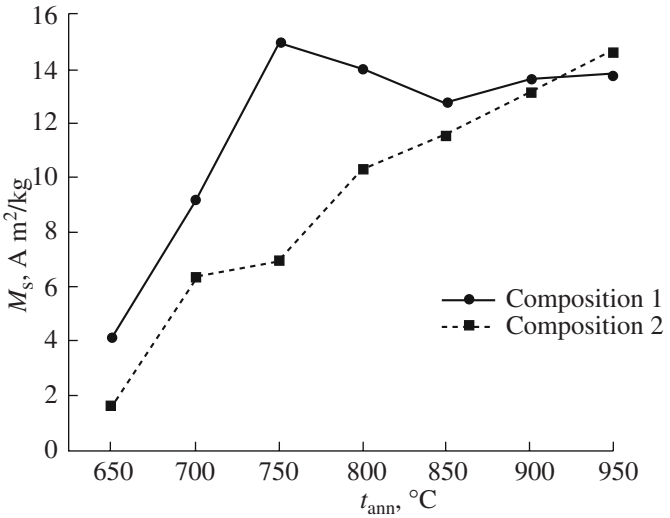

Fig. 2. Saturation magnetization as a function of annealing temperature for glass-ceramics 1 and 2.

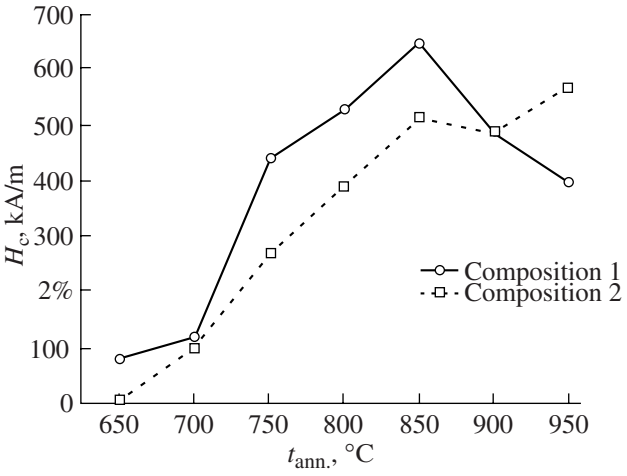

Fig. 3. Coercivity of the glass-ceramics as a function of annealing temperature.

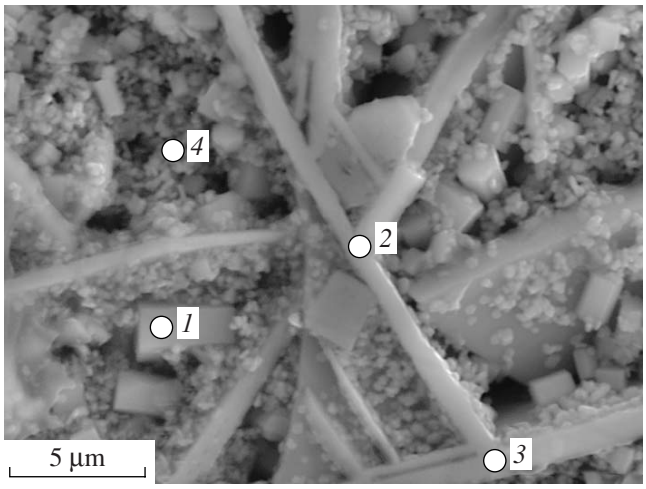

Fig. 4. SEM micrograph of the glass-ceramic 1 prepared at 950°C.

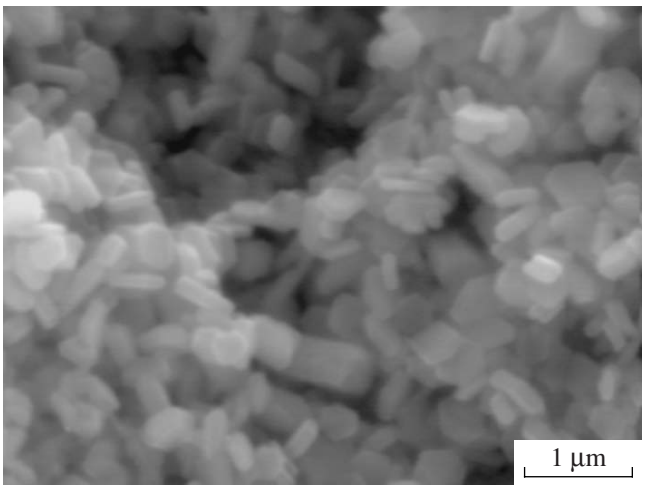

Fig. 5. SEM micrograph of the glass-ceramic 2 prepared at 950°C.

The saturation magnetization of glass-ceramic 1 increases with annealing temperature up to 750°C. At higher annealing temperatures, M_s first decreases slightly and then varies little. This can be accounted for by the increase in the degree of aluminum substitution for iron in $SrFe_{12-x}Al_xO_{19}$ with increasing temperature. The saturation magnetization of samples 2 rises steadily with annealing temperature. The most likely reason for the slower rise in magnetization in comparison with composition 1 is the presence of the antiferromagnetic phase $SrFeO_{3-y}$ [7], which prevails at low temperatures and gradually gives way to the hexaferrite as the heat treatment temperature is raised.

The coercivity of glass-ceramic 2 increases with annealing temperature, reaching 570 kA/m at 950°C. The H_c of samples 1 is a nonmonotonic function of annealing temperature, with a maximum (650 kA/m) at t_{ann} = 850°C. The rise in coercivity below this temperature is attributable to the increase in the size and thickness-to-diameter ratio of single-domain hexaferrite particles and the rise in the degree of aluminum substitution for iron in the hexaferrite [3, 8]. The most likely reason for the drop in the coercivity of samples 1 is that high-temperature annealing of these samples leads to the formation of large, multidomain hexaferrite particles [9], as will be shown below.

Table 3. X-ray microanalysis data for the glass-ceramic sample of composition 1 prepared at 950°C

Region in Fig. 4	Metal composition, at %			Phase
	Sr	Fe	Al	
1	34	11	55	$SrAl_2O_4$
2	12	62	26	$Sr(Fe,Al)_{12}O_{19}$
3	11	66	23	$Sr(Fe,Al)_{12}O_{19}$
4	7	81	12	$Sr(Fe,Al)_{12}O_{19}$

Figures 4 and 5 are SEM micrographs of the glass-ceramics prepared at 950°C. The particle diameter in the sample of composition 2 does not exceed the critical size for single-domain behavior of strontium hexaferrite (about 500 nm [10]). The sample of composition 1 consists not only of fine but also of large particles, which are missing at annealing temperatures from 650 to 850°C. Table 3 presents X-ray microanalysis data for different parts of this sample. The large platelike particles several microns in size are seen to be enriched in Fe, which implies that they consist of strontium hexaferrite. Their size markedly exceeds the critical size for single-domain behavior of strontium hexaferrite, and hence their coercivity is not very high. This sample has a wasp-waisted magnetic hysteresis loop, characteristic of materials consisting of both high- and low-coercivity particles [11, 12]. At the same time, the sample prepared at 850°C has a pot-bellied loop (Fig. 6). The formation of large particles in glass-ceramic 1 at 900 and 950°C may be associated with the presence of ferromagnetic nanoparticles in the as-prepared glass, which act as crystallization centers during heat treatment.

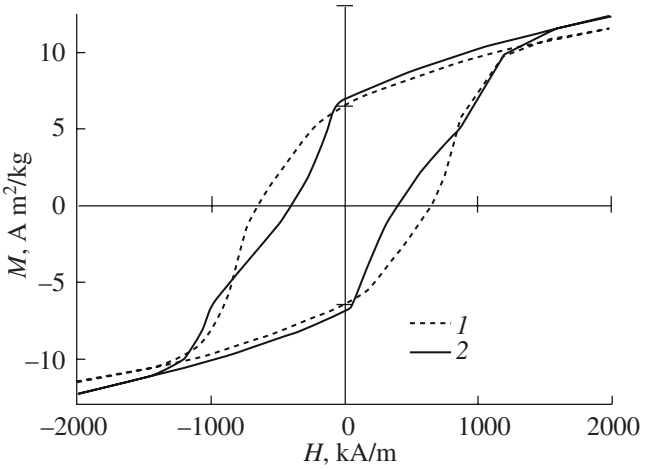

Fig. 6. $M(H)$ curves of glass-ceramics 1 prepared at (*1*) 850 and (*2*) 950°C.

CONCLUSIONS

We prepared glass-ceramics by heat-treating glasses with nominal compositions $11SrO \cdot 5.5Fe_2O_3 \cdot 4.5Al_2O_3 \cdot 4B_2O_3$ (1) and $15SrO \cdot 5.5Fe_2O_3 \cdot 4.5Al_2O_3 \cdot 4B_2O_3$ (2) at temperatures from 650 to 950°C, and determined their phase composition. The phases identified in the glass-ceramics are strontium orthoferrite, $SrFeO_{3-y}$; strontium aluminate, $SrAl_2O_4$; strontium borate, $Sr_2B_2O_5$; and strontium hexaferrite, $SrFe_{12}O_{19}$. Aluminum partially substitutes for iron in the structure of the hexaferrite. At high annealing temperatures, the degree of substitution in $SrFe_{12-x}Al_xO_{19}$ is $x = 2$ and $x = 1{,}3$ for compositions 1 and 2, respectively. The coercivity of the glass-ceramics reaches 650 kA/m for composition 1 and 570 kA/m for composition 2.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant nos. 07-03-00569-a and 08-03-91950-NNIO_a), the Deutsche Forschungsgemeinschaft (project no. 436 RUS 113/933/0-1), and the Federal Agency for Science and Innovations (subcontract for the state contract no. 02.513.11.3385).

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